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(54) Ultrahydrophobic zeolite Y

(57) Hydrothermally stable forms of zeolite Y which exhibit an unique degree of adsorptive preference for less polar organic molecules relative to strongly polar molecules such as water are prepared by rigorously steaming the low-sodium forms of zeolite Y.

The zeolite has SiO₂/Al₂O₃ ratio of 3.5-35, ion exchange capacity not greater than 0.070, unit cell dimension a₀ of less than 24.45 Å, surface area of at least 350m²/g, sorptive capacity for water vapour at 25°C and p/p₀ value of 0.10 or less than 5% wt and a Residual Butanol test value of not more than 0.40% wt.

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SPECIFICATION

Ultrahydrophobic zeolite Y

5 The present invention relates in general to modified forms of zeolite Y, and more particularly to highly thermally stable forms of zeolite Y which exhibit to an unique degree an adsorptive preference for less polar organic molecules relative to strongly polar molecules such as water. To nominally distinguish these novel compositions from those heretofore known, they are hereinafter called ultrahydrophobic type Y zeolites, or more briefly as UHP-Y.

10 In the main, the so-called hydrophobic zeolites are those species which have quite high framework molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, either as a result of synthesis conditions or by virtue of post-synthesis removal of aluminium atoms from the crystal lattice by chelation, extraction with acids, or other well-known techniques. No precise $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio for threshold hydrophobicity has been established or agreed upon in the art, but significant development of the property is generally evident when the ratio is 20 or higher. It has
15 been proposed that the hydrophobicity is attributable to the relative absence of cation "sites" which are associated with the framework AlO_4 -tetrahedra.

An apparent exception to the rule of correlation of hydrophobicity with high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios occurs in the case of the modified zeolite Y compositions of C.V. McDaniel and P.K. Maher denominated Z-14US and sometimes referred to as ultra-stable forms of synthetic faujasite. These compositions are described in detail
20 and the method for their manufacture disclosed in U.S.P. 3,449,070; U.S.P. 3,293,192; and "Molecular Sieves", p. 186, Society of Chemical Industry, London (1968). It is theorized by Maher and McDaniel that even though the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of Z-14US does not exceed 7, the hydrophobic character of the zeolite is due to the thermal destruction of the cation sites as a result of the rigorous high temperature calcination in air which is an essential part of the formative process. Whatever the reason, their experimental data establish that the
25 adsorption capacity of Z-14US for water at 25°C. and a water relative humidity of 10 percent is within the range of 6 to 12 weight percent based on the anhydrous weight of the zeolite. The thermal stability of Z-14US is maintained only if the Na_2O content is maintained at or below 1.0 weight percent.

In copending U.S. Application Serial No. 846,312 filed October 28, 1977 there is described another distinct modified form of zeolite Y which is highly stable in the hydrothermal sense and which is not dependent upon
30 a low sodium content for its stability. Briefly, this composition is prepared by calcining a hydrogen cation form of zeolite Y containing from 10 to 25 equivalent percent sodium cations in sufficient steam to prevent dehydroxylation at a temperature of from 550°C. to 800°C., and quickly cooling the product to below 350°C. The relatively high sodium content of the starting material prevents severe hydrolysis of the zeolite during steaming and avoids the elimination of framework AlO_4 -tetrahedra which occurs when low-sodium forms of
35 zeolite Y are steamed under these conditions. Possibly due to the relatively low ion-exchange capacity of the aforesaid steam stabilized compositions, some hydrophobic character is evident, but is less pronounced than in the Z-14US zeolites.

It has now been discovered that neither of the aforesaid stabilized forms of zeolite Y need be considered as ultimate products. On the contrary, it is found that both can serve as starting materials in the preparation of
40 an unique form of zeolite Y which not only retains the extraordinary stability of such precursors, but also exhibits a degree of hydrophobicity heretofore never observed in a molecular sieve of the Y-type. Accordingly, the zeolites of the present invention are called ultrahydrophobic type-Y zeolites or simply UHP-Y.

UHP-Y zeolites can be characterized to distinguish them from all other zeolite forms as being zeolitic
45 aluminosilicates having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of from 4.5 to 35, preferably 4.5 to 9, the essential X-ray powder diffraction pattern of zeolite Y, an ion-exchange capacity of not greater than 0.070, a unit cell dimension a_0 of from 24.20 to 24.45 Angstroms, a surface area of at least 350 m^2/g . (B-E-T), a sorptive capacity for water vapour at 25°C. and a p/p_0 value of 0.10 of less than 5.00 weight percent, and a Residual Butanol Test value of not more than 0.40 weight percent.

50 As used herein in this Specification and the appended claims, the following terms are intended to have the meanings set forth immediately below:

Surface areas of all zeolitic compositions are determined by the well-known Brunauer-Emmett-Teller method (B-E-T) (S. Brunauer, P. Emmett and E. Teller, J. Am. Chem. Soc. 60, 309 (1938)) using nitrogen as the adsorbate.

55 The essential X-ray powder diffraction pattern of zeolite Y is set forth in U.S.P. 3,130,007, issued April 21, 1964 and is incorporated by reference herein in its entirety. It will be understood by those skilled in the art that the shrinkage of the unit cell resulting from the present stabilization process will cause some slight shift in the d-spacings. In all events, the X-ray diffraction pattern of the UHP-Y compositions will exhibit at least the d-spacings corresponding to the Miller Indices of Table A below, and can contain all the other d-spacings
60 permissible to the face-centered cubic system with a unit cell edge of 24.20 to 24.45 Angstroms. The value of the d-spacings in Angstroms can be readily calculated by substitution in the formula:

$$\frac{a_0}{d_{hkl}} = \sqrt{h^2 + k^2 + l^2}$$

The X-ray pattern of the UHP-Y zeolites is obtained by standard X-ray powder techniques. The radiation source is a high intensity, copper target, X-ray tube operated at 50 Kv and 40 ma. The diffraction pattern from the copper K radiation and graphite monochromator is suitably recorded by an X-ray spectrometer scintillation counter, pulse height analyzer and strip chart recorder. Flat compressed powder samples are scanned at 1° per minute, using a 2 second time constant. Interplanar spacings (d) are obtained from Bragg Angle (2 theta) positions of peaks after subtracting background. The crystal symmetry is cubic.

TABLE A

10	Miller Indices hkl	Intensity I/I _o	10
	111	very strong	
	220	medium	
15	311	medium	15
	331	strong	
	333; 511	medium	
	440	medium	
	533	strong	
20	642	strong	20
	751; 555	strong	

The anhydrous state of any zeolite composition for purposes of determining constituent proportions in terms of weight percent is the condition of the zeolite after being fired in air at 1000°C. for one hour.

25 The term ion exchange capacity or IEC is intended to denote the number of active cation sites in the zeolite which exhibit a strong affinity for water molecules and hence appreciably affect the overall capacity of the zeolite to adsorb water vapor. These include all sites which are either occupied by metal or non-metal cations, or which are not occupied by any cation, but in any event are capable of becoming associated with sodium cations when the zeolite is contacted at 25°C. three times for a period of one hour each with a fresh aqueous ion exchange solution containing as the solute 0.2 mole of NaCl per liter of solution, in proportions such that 100 ml. of solution is used for each gram of zeolite. After this contact of the zeolite with the ion-exchange solution, routine chemical gravimetric analysis is performed to determine the relative molar proportions of Al₂O₃, SiO₂ and Na₂O. The data are then substituted in the formula:

$$35 \text{ IEC} = k[\text{Na}_2\text{O}/\text{SiO}_2] \quad 35$$

wherein "k" is the SiO₂/Al₂O₃ molar ratio of the zeolite immediately prior to contact with the NaCl ion-exchange solution.

The Residual Butanol Test is a measure of the adsorptive selectivity of zeolite adsorbents for relatively non-polar organic molecules under conditions in which there is active competition between water and less polar molecules for adsorption on the zeolite. The test procedure consists in activating the zeolite sample by heating in air at a temperature of 300°C. for 16 hours. Thereafter, the activated zeolite crystals are slurried with a solution of 1-butanol in water in proportions such that the slurry consists of 1.0 part by weight 1-butanol, 100 parts by weight water and 10 parts by weight of the as-activated zeolite. The slurry is mildly agitated for 16 hours while the temperature is maintained at 25°C. The supernatant liquid is then analyzed for its residual 1-butanol content in terms of weight percent.

For the determination of the sorptive capacity of the UHP-Y compositions for any particular adsorbate, for example water, the test zeolite sample is activated by preheating at 425°C. for 16 hours at a pressure of 5 micrometers of mercury in a conventional McBain apparatus. Thereafter, the temperature of the sample is adjusted to the desired value and contacted with the vapor of the test adsorbate at the desired pressure.

In the preparation of UHP-Y a number of different forms of zeolite Y can be used as starting materials. A particularly preferred starting composition is the low sodium form of the steam stabilized zeolite Y described and claimed in the aforementioned copending U.S. Application Serial No. 846,312, filed October 28, 1977.

That form of zeolite Y is prepared by the process which comprises providing an ion-exchange zeolite Y having the following composition in terms of mole ratios of oxides:
 0.75-0.9 (A)₂O:0.1-0.25 Na₂O:Al₂O₃:4.6-5.4 SiO₂:yH₂O wherein "A" represents H⁺ or NH₄⁺ or a mixture thereof, and wherein "y" has a value of from 0-9, heating the zeolite at a temperature between 550°C. and 800°C. for a period of at least 0.25 hour in an inert atmosphere comprising sufficient steam, preferably an atmosphere of pure steam at greater than 10 psia, to prevent dehydroxylation of the zeolite, removing at least a major proportion of any ammonia generated by the heated zeolite from contact with the zeolite, and cooling the steamed zeolite to a temperature below 350°C. at a rate sufficiently rapid that the cooled zeolite exhibits any X-ray powder diffraction pattern having the d-spacings corresponding to the Miller Indices, hkl, of 331 at least as strong in intensity as that corresponding to the Miller Indices 533, prior to any post-steaming ion-exchange treatment. Thereafter, the sodium content of the zeolite is reduced to below 0.5 weight percent as Na₂O on an anhydrous basis by conventional cation exchange with an ammonium salt such as

ammonium chloride.

Because the procedure of the present invention which imparts the ultrahydrophobicity to the zeolite products also tends to improve their hydrothermal stability, it is not essential that means used to lower the sodium content of the starting zeolite to below 0.5 weight percent be such that simultaneous thermal stabilization occurs. For this reason, it is not essential to include all of the precautionary steps of the steaming process of application Serial No. 846,312 in order to obtain a satisfactory low-sodium starting material for use in the process of the present invention.

In general, therefore, a suitable low-sodium starting material can be prepared by providing a zeolite Y having a composition in terms of mole ratios of oxides of:
 0.75-0.90 (A)₂O:0.1-0.25 Na₂O:Al₂O₃:4.5-6 SiO₂:yH₂O wherein "A" represents a H⁺ or NH₄⁺ cation or a mixture thereof and wherein "y" has a value of from zero to 9, heating the zeolite at a temperature of 550°C. to 800°C. for a period of at least 0.05 hour, preferably at least 0.5 hour, in the presence of at least 10 psia steam, thereafter cooling and ion-exchanging the steamed zeolite to replace sufficient of the residual sodium cations with hydrogen or ammonium cations to reduce the Na₂O content to below 0.5 weight percent on an anhydrous basis. This procedure is illustrated in Example 1 hereinafter.

It is feasible to reduce the sodium content of zeolite Y to below 0.5 weight percent without a calcination step, providing the ion-exchange procedure is carried out consecutively using a number of fresh ion-exchange media. This procedure is illustrated in Example 2 below.

Generally, it is found that the Z14-US compositions prepared by the so-called double calcination procedure of U.S.P. 3,293,192 and U.S.P. 3,449,070, both incorporated herein by reference, are suitable starting materials for the process of the present invention provided the calcination temperatures employed are not rigorous enough to reduce the surface area of the Z14-US products to below 400 m²/g. In the double calcination procedure, the first step is the reduction of the sodium cation content of a sodium zeolite Y having a SiO₂/Al₂O₃ molar ratio of 1.5 to 4.0 by ion exchange with an aqueous solution of an ammonium salt, amine salt, or other salt which on calcination decomposes and leaves the hydrogen cation. This exchange is carried out rapidly at a temperature between 25°C. and 150°C. using an exchange medium containing a stoichiometric excess of about 5 to 600 percent to attain a residual sodium level in the zeolite of from 1.5 to 4 weight percent, preferably less than 2.9 weight percent. The washed and dried product is then calcined in air mildly, preferably at a temperature in the range of 700°F. to 1000°F. for purposes of the present invention, to substantially deaminate the zeolite while avoiding the substantial dehydroxylation thereof. Subsequent ion-exchange with a salt solution as in the first ion-exchange procedure results in the reduction of the Na₂O content to below 0.5 weight percent as required for the starting material of the present invention. For purposes of this invention, it is preferred that the second calcination be limited to a temperature of from 300°C. to 600°C. or eliminated altogether. A preparation of this type is illustrated in Example 2 below.

In steaming the above-defined starting forms of zeolite Y to form the UHP-Y compositions of the present invention, the important process conditions are the temperature and pressure of the steam and the length of the steaming period. The steaming environment should contain at least 0.2 atmospheres steam and can be as high as about 10 atmospheres, or even higher. Preferably, a pure steam environment of from 0.25 to 1.0 atmospheres is employed. The steam can be used in admixture with gases inert toward the zeolite such as air, nitrogen, helium, hydrogen and the like, particularly when the steam pressure is less than one atmosphere.

In general, the higher the steam temperature and pressure, the shorter the time period required to transform the low-sodium starting materials to the ultrahydrophobic zeolite compositions of the present invention. Minimum steaming time is also dependent to some degree upon the particular starting zeolite employed and cannot, therefore, be set forth herein in terms of a mathematical relationship which is universally applicable. For example, using a steam pressure of about 1 atmosphere, it has been found that at 725°C. at least about 4 hours steaming time is required, but 16 hours is preferable. At 750°C. this minimum steaming time can be halved, and at 800°C. only about 0.5 hours is required. At 870°C. about 5 to 10 minutes steaming time can suffice, but these times are preferably longer by a factor of three or four to ensure optimum results. In any event, the efficacy of a given time, temperature, steam pressure and starting material can readily be validated by routine analysis of the product obtained to determine if the water adsorption capacity at 25°C. and 10 percent relative humidity is less than 5.00 weight percent and the Residual Butanol Test value is not greater than 0.40 weight percent. Unduly protracted steaming periods, i.e., greater than about 16 hours at 750°C. and 4 hours at 850°C., should be avoided since under the relatively rigorous steaming conditions imposed, the zeolite tends to lose structure and surface area due to hydrolytic side reactions.

The present compositions and the method for their preparation are illustrated in the following Examples:

EXAMPLE 1

60

(a) Preparation of a Low-sodium Zeolite Y starting Material.

A sample of air-dried ammonium exchanged type Y zeolite having a composition exclusive of water of hydration:

0.156 Na₂O : 0.849 (NH₄)₂O : Al₂O₃ : 5.13 SiO₂ was tableted into 1/2 inch diameter slugs and changed to a Vycor tube 24 inches in length and 2.5 inches in diameter and provided with an external heating means. Over

a period of 0.25 hours, the temperature of the charge was raised to 600°C. and thereafter maintained at this temperature for one hour. During this 1.25 hour period, a pure steam atmosphere at 14.7 psia generated from demineralized water was passed upward through the charge in the tube at a rate of 0.1 to 0.5 pounds per hour. Ammonia gas generated during the heating by deamination of the zeolite was passed from the system continually. At the termination of the heating period the steam flow through the tube was stopped and the temperature of the charge in the tube was lowered to ambient room temperature over a period of 5 minutes. Analysis of this composition indicated the characteristic X-ray powder diffraction pattern of zeolite Y, a surface area of 760 m²/g. and an a₀ value of 24.52 Angstroms. Thereafter the sodium cation content of the first steamed material was reduced to 2.0 equivalent percent (0.27 weight percent as Na₂O) by ion exchange using an aqueous solution of NH₄Cl (30 wt.-%) at reflux.

(b) Preparation of UHP-Y.

The low-sodium starting material prepared in part (a) supra was converted to the UHP-Y composition of the present invention using the same apparatus and conditions as in part (a) except that the pure steam calcination environment was passed over the sample in the reactor at 14.7 psia at a temperature of 800°C. for 4 hours. The product was cooled to ambient room temperature in a desiccator and portions thereof analyzed for ion-exchange capacity, B-E-T nitrogen surface area, adsorption capacity for water, nitrogen and n-hexane and Residual Butanol Test value. The data from the analyses are set forth below:

Adsorptive Capacity

Adsorbate	Pressure mm. Hg.	Temp., °C.	Loading, wt.-%
Nitrogen	35	-196	15.8
"	66	"	16.5
"	137	"	17.3
"	528	"	19.2
Water	2.0	25	3.1
"	4.6	"	4.6
"	20.0	"	15.0
n-Hexane	5.0	25	10.8
"	20.0	"	14.2
"	50.0	"	16.0
"	75.0	"	19.8
Ion-Exchange Capacity:	=	0.04	
Surface Area	=	530 m ² /g.	
Residual Butanol Test Value	=	0.23 weight percent	

EXAMPLE 2

(a) preparation of Low-sodium Zeolite Y Starting Material

A 150 gram sample of an ammonium-exchange zeolite Y containing 2.8 weight percent Na₂O and having a SiO₂/Al₂O₃ molar ratio of 4.9 was treated with a solution of 150 grams NH₄Cl in 1500 ml. water. The exchange solution-zeolite slurry was refluxed for one hour with moderate stirring, and the procedure repeated for a total of eight times. The zeolite was then washed chloride-free with distilled water and dried in air at room temperature. The Na₂O content of the product was 0.23 weight percent and the surface area (B-E-T) was greater than 900 m²/g.

(b) Preparation of UHP-Y

The low-sodium zeolite Y prepared in part (a) of this Example was converted to UHP-Y by treatment in pure steam at 14.7 psia at 800°C. for 4 hours using the apparatus described in Example 1. The product was analyzed to determine its hydrophobicity in terms of the Residual 1-Butanol Test, its ion exchange capacity, its surface area and its adsorption capacity for water at 25°C. The pertinent data are set forth below:

Residual Butanol Test Value	=	0.27 wt.-%
Ion Exchange Capacity	=	0.028
Surface Area (B-E-T)	=	450 m ² /g.

Water Adsorption Capacity
(25°C.)

$$= \begin{aligned} &p/p_o = 0.084; 3.02 \text{ wt.-%} \\ &p/p_o = 0.19; 4.03 \text{ wt.-%} \\ &p/p_o = 0.84; 22.8 \text{ wt.-%} \end{aligned}$$

5

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EXAMPLE 3

A low-sodium zeolite Y having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 6.4 and a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio of 0.2 was prepared (Example VIII of U.S.P. 3,449,070) by treating a 40 lb. charge of a zeolite Y (having an initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 5.42) with a solution of 80 lbs. of ammonium sulfate in 400 lbs. of water. The exchange solution was heated to a temperature of 100°C. for one hour with stirring. After this exchange the zeolite was filtered and washed in 50 lbs. of water containing 6 lbs. of ammonium sulfate. The zeolite was then returned to another solution containing 80 lbs. of ammonium sulfate in 400 lbs. of water for a second exchange. A third exchange using the same quantities of ammonium sulfate and water was effected. The zeolite was then rewashed by slurring three times in water, filtered, dried and calcined for 2 hours at 1500°F. at this point, the zeolite contained 2.08 wt.-% Na_2O . The final exchange of this zeolite product was effected by mixing ten pounds of the zeolite with a solution containing 30 lbs. of ammonium sulfate and 600 lbs. of water, at a temperature of 100°C. for one hour with stirring. The product was then filtered and washed free of sulfate, dried and analyzed. The chemical analysis was (wt.-%, dry basis):

20	Na_2O --- 0.2	20
	SiO_2 --- 77.1	
	Al_2O_3 --- 21.2	

25

The unit cell was found to be 24.44 Angstrom units and the surface area was greater than 600 m^2/g . This composition is converted to the UHP-Y of the present invention by calcining it in steam at a partial pressure of 10 psia for sixteen hours at a temperature of 750°C.

The UHP-Y compositions are especially suitable for use as adsorbents in applications where it is desired to preferentially adsorb organic constituents from solutions or mixtures thereof with water. For example, in the formation of synthesis gas by the distillation of coal, there is produced a condensate fraction which is principally water containing a relatively small proportion of phenol. For environmental and economic reasons the phenol is advantageously recovered from the condensate. This is readily accomplished by contacting the condensate at ambient room temperature with UHP-Y which selectively adsorbs the phenol. Desorption and recovery of the adsorbed phenol is accomplished by the well-known methods.

CLAIMS

1. Organophilic zeolitic aluminosilicate composition having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of from 4.5 to 35, the essential X-ray powder diffraction pattern of zeolite Y, an ion exchange capacity not greater than 0.070, a unit cell dimension, a_o , of less than 24.45 Angstroms, a surface area of at least 350 m^2/g ., a sorptive capacity for water vapor, at 25°C. and a p/p_o value of 0.10, of less than 5.00 weight percent, and a Residual Butanol Test value of not more than 0.40 weight percent.
2. Composition as claimed in claim 1 wherein the unit cell dimension is from 24.20 to 24.45 Angstroms.
3. Composition as claimed in claim 1 or 2 wherein the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is from 4.5 to 9.0.
4. Composition as claimed in claim 1, 2 or 3 wherein the Residual Butanol Test value is less than 0.30.
5. Composition as claimed in any one of claims 1 to 4, wherein the water adsorption capacity, at 25°C. and a p/p_o value of 0.10, is less than 4.0 weight percent.
6. Process for preparing a hydrophobic zeolite aluminosilicate composition which comprises providing a Y-type zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of from 4.5 to 6.0, not greater than 3.3 equivalent percent metal cations and having an adsorptive capacity for water vapor, at 25°C. and a p/p_o value of 0.10, of at least 6.0 weight percent and a surface area of at least 350 m^2/g ., and calcining said zeolite in an environment comprising from about 0.2 to 10 atmospheres of steam at a temperature of from 725°C. to 870°C. for a period of time sufficient to reduce the adsorption capacity for water vapor at 25°C. and a p/p_o value of 0.10 of less than 5.00 weight percent.
7. Process as claimed in claim 6 wherein the calcination is carried out in an environment of steam at about 1 atmosphere pressure and at a temperature of about 750°C. for a period of from about 2 to 16 hours.
8. Process as claimed in claim 5 wherein the calcination is carried out in an environment of steam at about 1 atmosphere pressure and at a temperature of about 800°C. for a period of from about 0.5 to 4 hours.
9. Process as claimed in any one of claims 6 to 8, wherein the Y-type zeolite starting composition is prepared by the procedure which comprises providing a zeolite Y having a composition in terms of mole ratios of oxides of:
0.75-0.90 (A) $_2\text{O}$:0.1-0.25 $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$:4.5-6 $\text{SiO}_2:y\text{H}_2\text{O}$ wherein "A" represents a H^+ or NH_4^+ cation or a mixture thereof and wherein "y" has a value of from zero to 9, heating the zeolite at a temperature of 550°C. to 800°C. for a period of at least 0.05 hour, in the presence of at least 10 psia steam, thereafter cooling and ion-exchanging the steamed zeolite to replace sufficient of the sodium cations to reduce the Na_2O content to

below 0.5 weight percent on an anhydrous basis.

10. An organophilic zeolitic aluminosilicate composition as claimed in claim 1, substantially as hereinbefore described in any one of the foregoing Examples.

11. Process as claimed in claim 6, for preparing a zeolitic aluminosilicate composition substantially as
5 hereinbefore described in any one of the foregoing Examples. 5